

Research Papers

ELEMENTAL MASS-BALANCE OF MATERIAL CARRIED BY MAJOR WORLD RIVERS

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(Received February 9, 1978; revision accepted July 10, 1978)

ABSTRACT

Martin, J. M. and Meybeck, N., 1979. Elemental mass-balance of material carried by major world rivers. *Mar. Chem.*, 7: 173–206.

An estimate of average river particulate matter (RPM) composition was based on analyses of more than 40 elements in the Amazon, Congo, Ganges, Magdalena, Mekong, Parana and Orinoco rivers, to which were added literature data for 13 other major world rivers, covering the whole spectrum of morphoclimatic features. Geographic variations of major elements in RPM are mostly linked to weathering types and to the balance between weathering rate and river transport. As a result of chemical erosion, Al, Fe and Ti are enriched in RPM with respect to the average parent rock, while Na, Ca, Mg and Sr are strongly depleted. These figures are directly related to the relative importance of dissolved and particulate transport in rivers; this has been computed for each of 40 elements. In order to study weathering on a global scale, the total observed elemental fluxes (dissolved + particulate) have been computed and compared to theoretical ones. The latter were derived from the elemental content in the average parent rock and the total quantity of weathered material, computed from the Al ratio in RPM and in parent rock. Observed and theoretical fluxes are balanced for the less mobilized elements (rare earths, Co, Cr, Cs, Fe, Mn, Rb, Si, Th, Ti, U and V) for which no enrichment relative to Al is noted in RPM, and for B, Ba, Ca, K, Mg, Na, Sr which are relatively depleted in RPM due to their high dissolved transport. Additional fluxes have been found for Br, Sb, Pb, Cu, Mo, Zn and are possible also for Ni and P. This is reflected by marked enrichments in RPM relative to Al for the poorly or moderately dissolved transports (Pb, Cu, Zn). Several hypotheses involving either the natural origin (volcanic dust, marine aerosols, geochemical fractionation) or the artificial origin (worldwide pollution) are discussed to explain these discrepancies, assuming river transport and weathering either to be in a steady state on a global scale or not. However, none of them can fully account for these additional fluxes. It is most likely that these excesses have multiple origins, anthropogenic or natural or both. The comparison between RPM and deep-sea clay compositions emphasizes the prime influence of river input on oceanic sedimentation of Si, Al, Fe, Ti, lanthanides, Sc, Rb, V, etc. A few elements such as Zn, Sb, occur in excess in RPM as compared to deep-sea clays; in order to balance this excess, a remobilization of these elements out of the sediment can be considered. Finally, the enrichment of Co, Cu, Mn and Ni in deep-sea clays compared to RPM is discussed and attributed to several sources and processes.

INTRODUCTION

Terrigenous material is mainly supplied from land to ocean by rivers. The total flux of dissolved and particulate matter carried by rivers is estimated to be $20 \cdot 10^{15} \text{ g year}^{-1}$, i.e., $15.5 \cdot 10^{15} \text{ g year}^{-1}$ for the solid load and $4.0 \cdot 10^{15} \text{ g year}^{-1}$ for the dissolved load (Livingstone, 1963; Holeman, 1968; Meybeck, 1976). This amount appears to be about ten times greater than that of glaciers, Antarctica included, and about a hundred times greater than the atmospheric dust fallout over the ocean (Goldberg, 1972). The worldwide composition of the major elements in the dissolved load is now well documented (Alekin and Brazhnikova, 1960; Livingstone, 1963; Meybeck, 1976) but the trace elements have been studied much less (Durum and Haffty, 1963; Turekian, 1969; Morozov, 1969; Konovalov, 1973; Gibbs, 1977). On the other hand, the chemical composition of river particulate material has received even less attention, despite some recent studies (Turekian and Scott, 1967; Moore, 1967; Morozov, 1969; Martin et al., 1973; Förstner and Müller, 1974; Trefry and Presley, 1976; Wagemann et al., 1977; Gibbs, 1977; Martin and Meybeck, 1978).

A knowledge of the particulate matter composition is of considerable importance in giving greater insight into crustal weathering processes on a global scale and in determining the elemental fluxes between land and ocean, and to compare the river-borne material with the oceanic suspended matter and deposited sediments (Strakhov, 1967; Garrels and Mackenzie, 1971).

This estimate of the composition of suspended matter in rivers is based on major and trace element analyses from seven major rivers: Amazon, Congo, Ganges, Mekong, Magdalena, Parana and Orinoco and on data obtained from the literature, concerning other major rivers including the Amour, Colorado, Columbia, Danube, Garonne, Mackenzie, Lena, Mississippi, Niger, Nile, Ob, Saint Lawrence and Yenissei. The main results from two previous publications on rare earths (Martin et al., 1976) and on major elements (Martin and Meybeck, 1978) have also been included here, for information and clarity.

Sampling procedures

An outline of sampling procedures is given in Table I. Whenever possible, large river-water surface samples of up to 300 l were collected. The Ganges sample was a freshly deposited mud taken on the river bank. Suspended matter was usually recovered by filtration through a 0.45μ Millipore filter except for two samples for which continuous centrifuging was used. In this first estimate the suspended-matter composition is considered to be representative of the total particulate load of rivers, i.e., the bed-load composition is assumed to be identical to that of suspended matter and of minor importance with regard to the total solid load.

TABLE I

Procedures for river particulate matter recovery

River	Date of collection	Location	Volume sampled (l)	Suspended matter separation	Sampled by
Amazon	Sept. 1968	Manaus	30	Millipore filter 0.45 μ	Sioli
Congo	July 1969	Brazzaville	30	Millipore filter 0.45 μ	Authors
	July 1970		180	continuous centrifugation	
	Nov. 1976	Matadi	30	Millipore filter 0.45 μ	
Ganges	March 1973	Allahabad	river bank	freshly deposited sediment	Krishnaswamy
Mekong	Sept. 1968 to June 1969	Phnom Penh	4 x 30	Millipore filter 0.45 μ	Carbonnel
Orinoco	July 1971	Mouth	10 x 2	Millipore filter 0.45 μ	Authors
Parana	1.12.1975	Santo Dome	65	continuous centrifugation	De Petris
Garonne	Nov. 1968	La Réole	30	Millipore filter 0.45 μ	Authors
Magdalena	July 1973	Barranquilla	2	Millipore filter 0.45 μ	Authors

Analytical procedures

The filtered residue and sediments recovered by centrifuging were ashed at 600°C for analysis. Analytical methods are given in Table II and further details are given in the corresponding references. The results described hereafter concern the bulk composition of suspended sediment which includes the various forms of particulate transport occurring in rivers.

Composition and variability of river particulate matter

Analyses of suspended matter in rivers are given in Table III for the Amazon, Congo, Ganges, Magdalena, Mekong, Parana and Orinoco rivers. Additional data from literature sources are given in the same Table. They concern the major rivers quoted below. Smaller rivers which have been intensively studied (e.g., the Garonne in France) or those located in tropical areas (e.g., the Narbada in India) have also been added. The references are as follows:

Amazon: Cr, Mn, Fe, Co, Ni and Cu from Gibbs (1977).

TABLE II

Analytical methods used for suspended matter from Amazon, Congo, Ganges, Garonne, Mekong, Orinoco, Parana and Magdalena

Analytical method used	Element	Reference
Instrumental neutron-activation analysis	Ag As Ba Br Ca Cd Ce Co Cr Cs Cu Er Eu Fe Gd Hf Ho K La Lu Mo Na Nd Pr Rb Sb Sc Sm Ta Tb Tm Yb Zn	Delcroix and Phillipot (1973) Phillipot (1970)
Atomic absorption analysis	Al Fe Mn Ca Mg Na K	
Colorimetry	Si Ti P	
Alpha spectrometry	U Th	Ku (1966)
U. V. spectroscopy	B Ba Cu Ga Mn Mo Ni Pb Sr V Zn	Kulbicki et al. (1967)

Amour, Lena, Ob, Yenissei: from Konovalov and Ivanova (1970) for Ag, Co, Cu, Mn, Ni, Pb, V and Zn; from Morozov (1969) for Cs, K, Li, Na and Rb.

Colorado: major elements from Gould (1960); Co, Cr, Mo, Ni from Turekian and Scott (1967); Cs, Li, Rb from Sreekumaran et al. (1968).

Columbia: Cs, Li, Rb from Sreekumaran et al. (1968).

Danube: major elements and trace elements, except Cs and Li, from Georgescu et al. (1973), deposited sediment, at Portita; for Cs, and Li from Morozov (1969).

Garonne: major elements from Martin et al. (1978a); B, Ba, Cr, Ga, Mo, Sr and V from Martin et al. (1973); rare earths from Martin et al. (1976); U and Th from Martin and Meybeck (1978). Cu, Ni, Pb and Zn from Etcheber et al. (1977).

Ganges: this study, except for Cu, Li, Zn, from Handa (1972)

Mackenzie: major elements and Cd, Co, Cr, Cu, Pb, Zn, suspended sediment from Wagemann et al. (1977); B, Li, Ni from Dewis et al. (1972).

Mississippi: Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn, three-year averages from Trefry and Presley (1976, tables 3–5); Ag from Turekian and Scott (1967); Ga from Brady and Cahill (1973); Mo from Bertine (1970).

Narbada: from Borole et al. (1977).

Niger: from Porrenga (1967): major elements sample Vsl 381; trace elements table 14.

Nile: major elements from Clarke (1924); B, Cu, Li, Zn from Ashry (1973) average of deposited sediment, samples DR1, DR3, DR4.

Saint Lawrence: from d'Anglejan (1973) and d'Anglejan and Smith (1973), values for the upper estuary.

Whenever possible all analyses have been expressed on an organic-matter-free basis, i.e., after ignition at 600°C. This has been achieved for the Amazon,

Congo, Ganges, Magdalena, Mekong, Orinoco, Parana, Nile, Danube, Niger, Mackenzie and Colorado samples but not for the samples from the other rivers due to lack of information.

It must be noted that according to Trefry and Presley (1976) the Al, Fe and Mn contents in the Mississippi are somewhat different from old analyses quoted by Clarke (1924) used in our previous paper (Martin and Meybeck, 1978).

Representativity of data

The selected rivers represent a wide spectrum of morphoclimatic features, ranging from subarctic to equatorial environments and from mountain rivers to plain rivers. The highly polluted rivers of western Europe or eastern U.S.A. have been discarded, however some contamination may still occur in some rivers such as the Saint Lawrence. The average contents listed in Table III are generally based on selection of rivers corresponding to about 25% of the continental area drained to the ocean and to 15% of the world river solid discharge. (It must be noted that this sample of rivers can lead to slightly biased results for certain trace elements which are usually measured in temperate and arctic rivers.)

The validity of data used in Table III is highly variable. As seen in Table I many rivers were sampled only once. However, for the major elements the suspended-load composition is not usually highly variable. A five-year survey of the Rhone (unpublished) showed that for 17 samples the coefficient of variation for these elements (s/\bar{x}) ≤ 0.3 , except for phosphorus. A similar observation has been made on four seasonal samples taken in the Mekong river, while Trefry and Presley (1976) found no important variation in the major-element content during a one-year study of Mississippi suspended matter. For trace elements, the variations observed in these studies are much higher, but in no case do they exceed one order of magnitude, i.e., the variations are far below those sometimes found from one river to another (Konovalov and Ivanova, 1970; this study). Average values for the Amazon (Co, Cu, Cr, Fe, Mn, Ni), Colorado, Mississippi, Ob, Lena, Saint Lawrence, and Mackenzie are based on results obtained during at least a one-year period.

World average composition of river particulate matter

The mean contents of the river suspended matter (Table III) have been estimated in two ways.

- (i) averages for major elements (Al, Ca, Fe, K, Mg, Mn, Na, P, Si, Ti) are weighted according to the suspended load as given in Meybeck (1976) i.e., values before construction of dams. As the new Mississippi and Niger data were not included in our previous estimates (Martin and Meybeck, 1978) there is a slight discrepancy between these two sets of values.
- (ii) the average contents for trace elements are median values. However Rb, Co, and Ni values for the Saint Lawrence have been discarded in this computa-

TABLE III

Elemental contents of world major rivers particulars

River	Ag	Al	As	Au	B	Ba	Br	Ca	Cd	Ce	Co	Cr
Amazon		115,000	5.3	0.25	68	700	54	16,000		112	41	193
Amour		43,000						34,000			17	82
Columbia												
Congo	38	117,000	3.8	0.04	43	790	10	8,400		90	25	175
Danube	<0.3	63,000						45,000		65	13	100
Ganges		77,000				490		26,500		98	14	71
Garonne		118,000			120	815		19,500		93	39	255
Lena												
Mackenzie		78,000			49			35,800	0.81		14	8.5
Magdalena			7.1				2	10,000			19	136
Mekong		112,000	27		87	600		5,900	2	93	20	102
Mississippi	0.7	88,000	14.6						1.4		21	72
Narbada		79,000										
Niger		156,000				260		3,300			40	150
Nile		98,000			75			40,000				
Ob	14										14	
Orinoco		113,000			50	270		3,000			10	70
Paraná		106,000	3.9	0.07			5	5,900			23	90
St. Lawrence	60	78,000						23,000			550	270
Yenissei	29										40	
Yukon											40	115

(10⁻⁶ g/g)

TABLE III (continued)

	Ag	Al	As	Au	B	Ba	Br	Ca	Cd	Ce	Co	Cr
River suspended matter (10^{-6} g/g)		94,000	5		70	600	5	21,500	(1)	95	20	100
Surficial rocks (10^{-6} g/g)		69,300	7.9	0.01	65	445	4	45,000	0.2	86	13	71
River dissolved matter (10^{-6} g/l)	0.3	50	1.7	0.002	18	60	20	14,600		0.08	0.2	1
Flux ratio	—	1.00	0.85	—	1.3	1.2	10	0.95		0.8	1.15	1.0
Dissolved transport index			0.13	44	38	19	90	62		0.2	2.5	2.5
Previous estimates suspended matter (10^{-6} g/g)	3(2)	80,000(1)						28,600(1)	18(2)		49(4) 60(2)	154(4) 190(2)
Deep-sea clays (10^{-6} g/g) (5)	0.1	95,000	13	0.003	220	1,500		10,000	0.23	100	55	100
Oceanic suspended matter, euphotic zone (10^{-6} g/g) (6)						126	100				13	
Oceanic suspended matter, deep ocean (10^{-6} g/g) (7)	9.3	7,500		1.3						35	15.3	173

TABLE III (continued)

	Cs	Cu	Er	Eu	Fe	Ga	Gd	Hf	Ho	K	La
River suspended matter (10^{-6} g/g)	6	100	(3)	1.5	48,000	25	(5)	6	(1)	20,000	45
Surficial rocks (10^{-6} g/g)	3.6	32	3.7	1.2	35,900	16	6.5	5	1.6	24,400	41
River dissolved matter (10^{-6} g/l)	0.035	10	0.004	0.001	40	0.09	0.008		0.001	1,350	0.05
Flux ratio	1.2	2.9	—	0.95	1.0	1.15	(0.6)	—	—	0.7	0.8
Dissolved transport index	1.4	19	0.3	0.2	0.2	0.9	0.4		0.3	14	0.3
Previous contents suspended matter (10^{-6} g/g)	5(3)	341(4) 2,500(2)			66,500(1) 59,360(4)					18,700(3) 20,000(1)	
Deep-sea clays (10^{-6} g/g) (5)	5	200	2.7	1.5	60,000	20		4.5	1	28,000	45
Oceanic suspended matter, euphotic zone (10^{-6} g/g) (6)		109									
Oceanic suspended matter, deep ocean (10^{-6} g/g) (7)		200		0.6	13,700	5					15

TABLE III (continued)

River	Li	Lu	Mg	Mn	Mo	Na	Nd	Ni	P	Pb	Pr
Amazon		0.6	11,200	1,030	0.7	7,850		105	1,650	105	
Amour								82		307	
Colorado	19		10,400	430	10	4,800		40	540		
Columbia	12										
Congo		0.37	5,800	1,400	4	2,100		74	1,500	455	
Danube	40	0.5	21,000	600	2.2	17,400		40	680	178	
Ganges	12.5	0.51	12,400	1,000	4	10,700	48	80	560		
Garonne		0.42	17,300	1,700	3	5,600	36	33	1,300	381	8.2
Lena								147			
Mackenzie	22		4,000	600		2,200		22		24	
Magdalena						7,700					
Mekong		0.58	13,500	940	2	5,200	47	99	2,000	113	8.5
Mississippi	38			1,300	5.1			55		45	
Narabada				1,200				85			
Niger			9,300	650		900		120	1,600		
Nile	25		18,500			7,300		124		65	
Ob	86					10,900		30		76	
Orinoco			5,800	740							
Paraná		0.57	10,900	270		6,700			1,300		
St. Lawrence			24,500	700		25,000		240		670	
Yenissei								325		263	
Yukon				1,270				136			

(10⁻⁶ g/g)

TABLE III (continued)

	Li	Lu	Mg	Mn	Mo	Na	Nd	Ni	P	Pb	Pr
River suspended matter 10 ⁻⁶ g/g	25	0.5	11,800	1,050	3	7,100	35	90	1,150	150	(8)
Surficial rocks (10 ⁻⁶ g/g)	42	0.45	16,400	720	1.7	14,200	37	49	610	16	9.6
River dissolved matter (10 ⁻⁶ g/l)	12	0.001	3,800	8.2	0.5	5,100	0.04	2.2	40	1.0	0.007
Flux ratio	0.95	0.85	0.95	1.1	1.8	1.0	0.7	1.4	1.5	7	—
Dissolved transport index	50	0.5	40	2.0	30	63	(0.3)	5	8	2	(0.2)
Previous contents suspended matter (10 ⁻⁶ g/g)	59(3)		14,000(1)	1,150(4) 430(2)	220(2)	11,000(1) 9,500(3)		120(4) 160(2)			
Deep-sea clays (10 ⁻⁶ g/g) (5)	45	0.5	18,000	6,000	8(5)	20,000	40	200	1,400	100	9
Oceanic suspended matter, euphotic zone (10 ⁻⁶ g/g) (6)				529						58	
Oceanic suspended matter, deep ocean (10 ⁻⁶ g/g) (7)		0.5								573	

TABLE III (continued)

River	Rb	Sb	Sc	Si	Sm	Sr	Ta	Tb	Th	Ti
Amazon	138	1.9	18	267,000	9.7	309	2.0		13	7,000
Amour	15			362,000						3,000
Colorado	6.6									
Columbia	60	1.0	12	239,000		61	1.1	1.6	16.2	8,400
Congo	200	1.9	16	299,000	6.3			0.62	15.7	4,200
Danube	116		11.5	285,000	9.7		1.25	0.7	17.5	5,300
Ganges				270,000	6.2	164		0.9	13	5,000
Garonne										
Lena				295,000						4,300
Mackenzie	42	2.4	21		6.7				12.6	
Magdalena	190	3.2	19.5	275,000	5.4	92	1.35	0.9	17	3,600
Mekong									10	
Mississippi										
Narbada				230,000		40				8,200
Niger				244,000						
Nile										
Ob	100									
Orinoco				292,000		83			15.8	8,600
Paraná	100	3	25.4	289,000	9.1	150	1.1		15.7	9,400
St. Lawrence	2,300			253,000		70				7,800
Yenissei										
Yukon										

(10⁻⁶ g/g)

TABLE III (continued)

	Rb	Sb	Sc	Si	Sm	Sr	Ta	Tb	Th	Ti
River suspended matter (10^{-6} g/g)	100	2.5	18	285,000	7	150	1.25	1.0	14	5,600
Surficial rocks (10^{-6} g/g)	112	0.9	10.3	275,000	7.1	278	0.8	1.05	9.3	3,800
River dissolved matter (10^{-6} g/l)	1.5	1.0	0.004	5,420	0.008	60		0.001	0.1	10
Flux ratio	0.7	4.3	1.3	0.8	0.75	0.8		0.7	1.1	1.1
Dissolved transport index	3	45	0.06	4.4	0.3	41		0.3	2	0.4
Previous contents suspended matter (10^{-6} g/g)	122(3)			302,000(1)						
Deep-sea clays (10^{-6} g/g) (5)	110	0.8	20	283,000	7.0	250	1.0	1.0	10	5,700
Oceanic suspended matter, euphotic zone (10^{-6} g/g) (6)										
Oceanic suspended matter, deep ocean (10^{-6} g/g) (7)		10.7	1.3		0.6					

TABLE III (continued)

River	Tm	U	V	Yb	Zn
Amazon		2.5	232	3.7	426
Amour			81		511
Colorado					
Columbia					
Congo		3	163	2.6	400
Danube			45	4.6	91
Ganges	0.35	2.8		3.2	163
Garonne	0.44	3.6	150	2.8	874
Lena			61		
Mackenzie					126
Magdalena				3.7	
Mekong	0.45	5.8	175	3.2	300
Mississippi					184
Narbada					
Niger			180		
Nile					93
Ob			173		
Orinoco		4.5	127		119
Paraná				3.5	
St. Lawrence					350
Yenisei			322		
Yukon					
(10 ⁻⁶ g/g)					

TABLE III (continued)

	Tm	U	V	Yb	Zn
River suspended matter (10^{-6} g/g)	(0.4)	3	170	3.5	350
Surficial rocks (10^{-6} g/g)	0.5	3	97	3.5	127
River dissolved matter (10^{-6} g/l)	0.001	0.04	1.0	0.004	30
Flux ratio		0.75	1.3	0.75	2.3
Dissolved transport index	(0.7)	3	1.4	0.3	17
Previous content suspended matter (10^{-6} g/g)					950(2)
Deep-sea clays (10^{-6} g/g) (5)	0.4	2.0	150	3	120
Oceanic suspended matter, euphotic zone (10^{-6} g/g) (6)			63		220
Oceanic suspended matter deep ocean (10^{-6} g/g) (7)		3.0			1,000

(1) Garrels et al. (1973); (2) Aston and Chester (1976); (3) Morozov (1969); (4) Gibbs (1977); (5) from Wedepohl (1960), Horn and Adams (1966), Bertine (1970), Hogdahl (1970), Fairbridge (1972), Piper (1974), and Chester and Aston (1976); (6) Chester and Stoner (1975); (7) Buat-Menard and Chesselet (1978), and Darcourt-Rieg (1973).

tion because of possible pollution.

Because of the scarcity of data and/or the wide variation of concentrations, (sometimes more than one order of magnitude) the average contents for Cd, Er, Gd, Ho, Pr, and Tm, must be considered as a first approximation.

The suspended material is compared in Table III with the average composition of the surficial rocks exposed to weathering, computed on the basis of a proportion of 52 shales, 15 sandstones, 7 limestones and 26 composite igneous rocks (Leopold et al., 1964). The elemental compositions chosen for this computation are those given by Green in Fairbridge (1972) for sandstone and limestone, Herrman (1970) for rare earths, Wedepohl (1968) for the magmatic rocks of the upper continental crust and for shales. Exceptions are made for Br and Ta which are taken from Green (1972) and Lu and Hf, from Horn and Adams (1966).

The comparison between the average river particulate matter and the averages which are taken from surficial rock will be discussed in detail below. It is, however, obvious that, due to the importance of the chemical weathering and resulting dissolved transport, the particulate material must be relatively enriched in the less soluble elements such as Al, Ti, Fe, Th, etc., and depleted in the more soluble Ca, Mg, Na etc.

Comparison with previous estimates

Previous estimates of average chemical composition of river-borne particulate have been given by Morozov (1969) for alkaline elements, by Aston and Chester (1976) for some trace elements and by Garrels, Mackenzie and Hunt (1973) for major elements. In a recent study Gibbs (1977) has set up a world average for transition elements based on two rivers, the Amazon and the Yukon. These values are reported in Table III. Although Garrels et al. have based their estimate on a restricted number of rivers, their values are very similar to ours. Our values for the alkaline elements are in very close agreement with Morozov's averages, although this author has only worked on rivers in the USSR. There is a major discrepancy between our values and those compiled by Aston and Chester, particularly for Cu, Mo, Cd which in their estimation are one order of magnitude higher. This difference is probably due to the inclusion of some rivers much smaller than ours that may be subject to local pollution. Finally, Gibbs' averages for Cr, Co, Ni, Fe, Mn and Cu based on the Amazon and the Yukon are very similar to ours.

Geographical variability of suspended matter composition

The geographical variability of elements in the suspended matter differs widely from one element to another. The most constant elements, for which the coefficient of variation s/\bar{x} is less than 0.2, are mostly the rare earths (Ce, Eu, La, Lu, Sm, Yb) and Si and Th. Aluminium, Fe, K, Ga, Hf, Sc, Ta, Ti, U, do not vary much ($0.2 < s/\bar{x} < 0.35$). On the other hand, As, Cr, Mg and Na vary moderately ($0.55 < s/\bar{x} < 0.7$) while Ca, Cs, Cu, Li, Mo, Ni, Pb,

Sr vary and Zn are highly variable ($s/\bar{x} > 0.7$). For the other elements s/\bar{x} is between 0.35 and 0.55. It is extremely interesting to note that the most constant elements are, in general, essentially carried in rivers by the particulate matter. The highly variable elements are those either carried mostly in solution (Ca, Na, Mg, As, Sr, Li), or significantly enriched in the suspended material (Zn, Pb, Mo, Cu) as will be seen later.

As previously noted, the variations of the major chemical elements (Al, Fe, Mg, Ca, Na, Si, Ti) can be fully explained by the climatic features in the river basins. There appear to be two different types of rivers according to the intensity of the weathering action, past and present (Martin and Meybeck, 1978). The contents of Al, Fe and Ti in the suspended matter of the tropical rivers are the highest, while the contents of Ca and Na are the lowest. For these rivers the particulates mainly originate from soil material enriched in insoluble rather than the more soluble elements which have been leached away. On the contrary, the contents of Al, Fe and Ti in temperate and arctic rivers are much lower, while the contents of Ca are higher. As the suspended load of these rivers is mainly derived from rock debris or poorly weathered particles, particularly in mountainous areas, the average composition of their particulates is much closer to the average content of surficial rocks. Similar results have been reported for Soviet rivers by Alekin and Brazhnikova (1968).

Relative importance of dissolved and particulate transports

In order to compare the dissolved and suspended loads, an average world value of dissolved major and trace elements in rivers is presented in Table III on the basis of the works of Turekian (1971) for Ag, Au, Ga, Sc and U; Bertine (1970) for Mo and Cr; Stumm and Morgan (1970) for total dissolved phosphorus; Gibbs (1975) for Fe and Al; Konovalov (1973) for B, Br and Ni; Konovalov (1973) and Turekian (1971) for Mn, V, Cu and Zn; Kharkar et al. (1968) for Co and Sb; Morozov (1969) combined with Kharkar et al. for Cs and Rb; Moore (1967) for Th; Boyle and Jonnasson (1973) for As; Durum et al. (1960) for Ba, Ti and Sr (arithmetic average of several rivers); Servant (personal communication) for Pb. The Li value given by Morozov (1969) seems to be much too low and the average value given by Heier and Billings (1969, p.3.1.1) although five times greater has been preferred.

It must be noted that the dissolved Al and Fe contents used here are about ten times lower than previous estimates from Durum et al. (1960), who used a 2μ pore-size filter, or from Livingstone (1963). This pore-size effect is now well established for these elements (Kennedy et al. 1974). It is likely that for iron the value quoted here does not correspond to a true solution but to very fine colloidal iron hydroxides which are eventually precipitated or adsorbed onto the particulate matter in estuaries. The final input of dissolved iron to the ocean may therefore be lowered by a factor of two or three (Figueres et al., in press).

The dissolved contents of rare earths of the Garonne River (Martin et al.,

1976) have been used for this first approximation as a world average. Although these values may not be representative on a global scale, they are direct measurements in good agreement with Turekian's estimates based on theoretical considerations (1971), with the exception of Ce.

Dissolved values of major elements (Ca, K, Mg, Na, Si) are natural values obtained by subtracting an estimate of the pollutant load of rivers from the total dissolved river load as given in a previous publication (Meybeck, 1977).

For each individual element the ratio of dissolved transport to total transport, the so-called *Dissolved Transport Index* (DTI), has been computed (Table III). This computation is based on the average dissolved content of rivers as stated above and on a world river discharge to the ocean of $37400 \text{ km}^3 \text{ year}^{-1}$ (Baumgartner and Reichel, 1975). The reliability of these DTI values is generally no better than 20%.

The DTI values shown in Table IV are in decreasing order and include data on S, Cl, N, F and I, using their mean value in shales (Wedepohl, 1968) as representative of the river particulate matter content. This approximation is validated by the marked similarity between shales and river suspended material for most elements. The dissolved contents used for these computations are from Livingstone (1963) for N, from Konovalov (1973) for I and F, and from Meybeck (1977) for S and Cl. These estimated DTI values (80% for S; 75% for Cl; 85% for I; 50% for N and 20% for F) should be confirmed by direct measurements.

The Dissolved Transport Index is the expression of the global vulnerability, for a given element, in the earth's outcropping rocks, rather than an estimate of solubility. Strakhov (1967) has also defined it as the relative mobility of elements in the weathering mantle. A few elements (S, Cl, Br, I, Ca, Na, Sr and Sb) are carried mainly by surface waters in the dissolved form. On the contrary Al, Fe, Ga, Hf, Sc, Ti and the rare earths are almost entirely carried to the ocean by the river particulate matter ($\text{DTI} < 1\%$). It is difficult to relate the DTI values to particular chemical properties, for this implies a knowledge of the relative abundance at the surface of the continents of the various minerals which contain the forty elements studied here, and of the chemical characteristics of these compounds, such as the solubility products. As this cannot be achieved, we have looked for similarities between the DTI order of Table IV and some well-known geochemical characteristics of the elements.

The elements which are the most easily washed away in solution from the continental surfaces are those which have either a marked metallic (Na, Ca, Li, Sr) or metalloïdic character (N, S, Cl, Br, I). This is generally related to the ionic potential of elements as given by Rösler and Lange (1972): high DTI values correspond either to the lowest ionic potentials ($\Phi < 2.02$) such as K, Na, Li, Sr, Ca or to very high potentials ($\Phi > 9.66$) for Mo, As, B and S. This is not a very close fit, as numerous exceptions are noted in the intermediate potentials for Zn^{2+} , Cu^{2+} , Mg^{2+} and Sb^{3+} which have DTI values

between 17% and 40%, or in the extreme potentials for Cs, Rb and P. Concerning the transport of alkali metals and alkaline-earth metals, the decreasing order of the DTI is very similar to that of relative hydrated ionic radii as given by Heier and Billings (1969): $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$ and $\text{Mg} > \text{Ca} > \text{Sr} > \text{Ba}$, however the DTI order is inversed for Li and Na, and for Mg and Ca. These results are in excellent agreement with Morozov's estimates of DTI for Na, K, Rb, Cs and Li in the USSR, and with Gibbs' data on transition elements in the Amazon and Yukon rivers. It must be noted here that the DTI values depend on the total amount of suspended matter carried by rivers to the oceans. Our values are based on a present-day estimate and are therefore different from the DTI values which can be computed from Table II of Garrels et al. (1973), based on "geological fluxes".

It is very important to note that these DTI values are averaged on a global scale and that wide geographic variations can be observed. From the study of major elements in individual rivers we have found that the DTI value for one given element could vary more than one order of magnitude according to the relief and climatic characteristics of the river basins which play a fundamental role in sediment supply and in chemical weathering. For example, the DTI value for Si can vary from 0.3% in the Colorado to 30% in the Congo (Martin and Meybeck, 1978).

However, the DTI order is slightly different from Strakhov's order of relative mobility (1967, p. 28) established for Soviet rivers, particularly for iron, due to the filter pore-size effect on contents of dissolved iron.

Elemental river fluxes to the ocean

Computation of observed and theoretical fluxes

A knowledge of the elemental composition of river particulate material is necessary to elucidate the weathering and transport processes at the continents' surface and to determine whether the erosion process is in a steady state at present or not (i.e., the rate of production of material during weathering is equal to the rate of total dissolved and solid material transport by rivers). The observed total transports are compared to theoretical fluxes assuming that land erosion is the only source of material to rivers. Therefore, this implies that, if the observed and theoretical fluxes are similar, all weathering products are carried entirely by rivers and that rivers only transport material originating from land denudation. If not, there are three possibilities:

- (i) the system is still in a steady state but an additional source of material must be found (e.g., volcanism, sea-salt particles);
- (ii) there is not a steady state at the continents' surface, either due to a present gradual increase of the soil layer or to a geochemical fractionation of certain elements in the soil profile;
- (iii) there is a worldwide pollution problem which can be seen in the river elemental transport. This process would not yet have reached a steady state.

Ideally, comparisons should have been made between observed and theoretical fluxes for each individual river as has been done in some local weathering studies (Gac and Pinta, 1973). However, this was not possible here for several reasons: e.g., the lithology and relief of the basins under study should be as homogeneous as possible, but if not, the amount of suspended matter originating from each sub-basin should be known and taken into account. As an example, Gibbs (1967) calculated that 47% of the solid load of the Amazon comes from the upper basin which corresponds to only 13% of the basin area. Sufficient information on the lithological and chemical composition of each basin, together with the origin of the suspended matter, was lacking in our study; therefore the river material and the surficial rocks have been compared only on a global scale.

The theoretical fluxes Φ_{th} have been computed on the basis of the ratio between the contents of a given conservative element in the suspended matter and in the surficial rock. Aluminium, which is commonly measured, is poorly soluble and, as yet, not affected by pollution, is usually chosen for this purpose.

It must be noted that titanium could also have been used for this calculation, but its average contents are much less accurately known than those of Al. The choice assumes that Al has reached a steady state at the continental surface, i.e., is not at present being accumulated by the soil layer, and is derived only from land erosion. For one given element x the theoretical flux to the ocean is:

$$\Phi_{thx} = [x]_{fr} M_{pm} [Al]_{pm} / [Al]_{fr}$$

where $[x]_{fr}$ = average content of element x in the surficial fresh rock,

$[Al]_{pm}$ = average Al content in river particulate matter,

$[Al]_{fr}$ = average Al content in the surficial fresh rock,

M_{pm} = annual river particulate discharge to the ocean.

The total suspended load M_{pm} is estimated to be $15\,000 \cdot 10^6 \text{ t year}^{-1}$ (Meybeck, 1977) and the ratio $[Al]_{pm}/[Al]_{fr}$ is $9.40/6.93 = 1.36$. Therefore, the total amount of fresh rock (M_{fr}) from which the river dissolved and particulate products are derived should be around $21\,000 \cdot 10^6 \text{ t year}^{-1}$. The difference between M_{fr} and M_{pm} — around $5.500 \cdot 10^6 \text{ t year}^{-1}$ — should be due to the total dissolved transport of material deriving from chemical denudation M_d which is roughly around $2.500 \cdot 10^6 \text{ t year}^{-1}$ if that part of the HCO_3^- carried by rivers originating from atmospheric CO_2 is removed. There is therefore an important discrepancy between the M_d derived from the Al-content ratio and the M_d derived from the direct measurement of river transport. This may be due to accumulation of the coarser detrital material within the basins, to poor estimation of present-day river suspended load, or to a non-steady-

state system, i.e., the river suspended material does not correspond to present chemical denudation, but derives from older soil layers. Finally, it could be due to differential weathering of various types of rocks. It is not possible at the present stage of this study to state which processes are relevant; therefore we will not consider the absolute fluxes, which are still questionable, but solely the *flux-ratio* (FR) between the theoretical flux Φ_{thx} and the observed flux $\Phi_{obs x}$.

$$\Phi_{obs x} = [x]_{sol} Q + [x]_{pm} M_{pm}$$

where $[x]_{sol}$ = average dissolved content of element x in rivers, Q = annual river water discharge to the ocean ($37\,400\text{ km}^3\text{ year}^{-1}$ according to Baumgartner and Reichel, 1975). Thus the flux ratio is:

$$FR = ([x]_{sol} Q + [x]_{pm} M_{pm}) ([x]_{fr} M_{pm} \cdot [Al]_{pm}/[Al]_{fr})^{-1}$$

The flux ratio has been computed for each element for which at least four values in rivers were available (see Table III). For this reason FR values for Au, Gd, Er, Ho, Pr, Tm are not computed or given as very rough estimates only. As there is considerable uncertainty in the FR value, and considering the coefficients of variation of the elements, it will be considered here that the flux ratio is not significantly different from unity if it is between 0.7 and 1.5.

It is noteworthy that when the dissolved flux is negligible as compared to the particulate flux, i.e., when the Dissolved Transport Index is below 10%, FR becomes the enrichment factor (EF) of the element in the river particulate matter (pm) taking into account only the elemental contents in the solid

$$\text{material and the fresh rock (fr): } EF = \frac{[x]_{pm}/[Al]_{pm}}{[x]_{fr}/[Al]_{fr}}$$

TABLE IV

Dissolved Transport Index (DTI) in rivers

Percentage of dissolved transport over total transport (ranked in decreasing order)

90–50%	Br, I*, S*, Cl*, Ca, Na, Sr
50–10%	Li, N*, Sb, As, Mg, B, Mo, F*, Cu, Zn, Ba, K
10–1%	P, Ni, Si, Rb, U, Co, Mn, Cr, Th, Pb, V, Cs
1–0.1%	Ga, Tm, Lu, Gd, Ti, Er, Nd, Ho, La, Sm, Tb, Yb, Fe, Eu, Ce, Pr, Al

*Estimates based on elemental contents in shales

Such EFs have also been used for oceanic suspended matter and for atmospheric aerosols (Duce et al., 1975) (Buat-Menard and Chesselet, 1978, 1979).

Balanced fluxes ($0.7 < FR < 1.5$)

The following poorly soluble elements have a flux ratio near unity: Ce, Co, Cr, Cs, Eu, Fe, Ga, La, Mn, Nd, Ni, P, Rb, Sc, Si, Sm, Tb, Th, Ti, U, V, Yb.

In this case their EF in the suspended matter is also near unity.

For the more soluble elements, B, Ba, Ca, K, Mg, Na, Sr (DTI > 10%) the observed flux through rivers is equal to the theoretical one. The detailed balanced fluxes of some elements are given in Table V.

If it is supposed that Al has reached a steady state during weathering and transport processes, then these elements have also reached a steady state at the continent's surface.

TABLE V

Estimates of some elemental river fluxes to the ocean (10^{12} g year⁻¹)

	Ca	Na	Mg	Si	Fe	Cu	Pb	Zn
River particulate load (1)	345	110	209	4430	733	1.55	2.3	5.4
River dissolved load (2)	495	131	129	203	1.5	0.37	0.04	1.1
Total river load	840	241	338	4630	734	1.9	2.3	6.5
Theoretical load (3)	946	298	345	5780	754	0.67	0.33	2.6
Discrepancy (4)	N.S.	N.S.	N.S.	N.S.	N.S.	+1.2	+2.0	+3.9
World mining production (5)	—	—	—	—	—	4.4	3.0	3.9

(1) Based on average contents (Table III) and total river particulate load of $15.5 \cdot 10^{15}$ g year⁻¹.

(2) Based on Meybeck (1977) plus corrections for Ca, Na, Mg, to eliminate pollution loads, oceanic salts and dust fallout. For Fe, Pb, Cu, Zn based on average dissolved contents (Table III) and $37400 \text{ km}^3 \text{ year}^{-1}$ for the river discharge.

(3) Based on average surficial rock contents (Table III) and a theoretical value of $21.1 \cdot 10^{15}$ g year⁻¹ for the total amount of parent rock affected by weathering at the continent surface drained by rivers to the ocean.

(4) N.S. = Not significant.

(5) Anonymous (1970).

Unbalanced fluxes

The situation of an unbalanced flux is only noted for elements carried in excess by rivers for which the flux ratio is greater than 1.5.

Additional fluxes are observed either for poorly soluble elements, such as Pb, or for the more soluble elements Br, Cu, Mo, Sb, and Zn. Although not significant, a similar figure can be forecast for Ni and P. It is important to note that such an additional input could not have been observed for the more soluble elements if only the EF had been used. As previously mentioned, several origins may be looked for, but first of all we must consider contamination of the river suspended matter during sampling, pretreatment and analysis. Since the flux ratios have been computed with data sampled from different rivers and analyzed by different methods and reported by several authors, this contamination is unlikely although not impossible, especially for lead.

The excess fluxes may also be artefacts due to differential erosion processes.

River particulates originate mainly from rocks which are easily eroded by mechanical erosion. However, trace-element contents in these types of rocks, such as shales, are not high enough to account for the high values measured in the suspended matter. River suspended matter originates mainly from mountainous areas where, on the global scale, the occurrence of elements such as Cu, Pb and Zn is higher (Wilson and Laznicka, 1972; Rona, 1977). Therefore, the excess transport in rivers could be an artefact due to the underestimation of the average composition of surficial rocks effectively exposed to erosion. The weathering process would then be at a steady state, and the fluxes balanced.

If there is no artefact, three possibilities remain: worldwide pollution, a non-steady state between weathering and transport processes, and finally a steady-state system implying additional natural sources to river material other than land erosion.

Worldwide pollution. The high fluxes found for Cu, Mo, Br, Sb, Pb, Zn could result from industrial activities either through direct release as particulates and/or dissolved elements (eventually adsorbed onto the finest particles), or through atmospheric particulate or dissolved contamination. This river contamination is widespread and well documented in industrial countries; it has been observed in deposited sediments from regional seas such as the Baltic (Erlenkeuser et al., 1974), lakes such as the Great Lakes (Kemp and Thomas, 1976), and rivers, for instance in Germany (Förstner and Müller, 1974).

Moreover the influence of man on elemental abundances has been also reported in remote areas such as Greenland and Antarctica (Murozumi et al., 1969; Weiss et al., 1971).

According to Lantzy and Mackenzie (1979), an important part of trace metals found in atmospheric rainout is due to industrial particulate emissions and fossil-fuel burning. This input is particularly important for Pb, Mo, Sb, As, Zn, Cd and Cu. However, this anthropogenic source cannot account for all the Cu and Zn excess found here in rivers, and elements such as As and V which are released into the atmosphere by industrial and urban pollution have not been found in excess in river transport.

Another way to check possible worldwide contamination is to compare the additional flux in rivers given in Table V with the world yearly production (Anonymous, 1970). For Cu, Pb and Zn the excess would represent from 25 to 75% of the present world production of these metals. If pollution can partly explain these additional fluxes, for example, the widespread use of P fertilizers and of Pb as an anti-knock product in gasoline, such a percentage is hardly credible and it seems necessary to look also for natural processes.

There is already a good deal of evidence of natural variations, sometimes reaching one order of magnitude, in Cu, Pb, Zn and Ni contents of deposited sediments from the Rhine and Weser rivers (Förstner and Müller, 1974, p. 58) and Lake Mutnoye (Gribovskaya et al., 1971), prior to the industrial era.

Non steady-state system. This may occur only if transport processes do not balance weathering: there is a continuous accretion of the weathering profile and the particles carried by rivers mainly originate from soil erosion. However, since we have normalized all fluxes to Al, excess fluxes for some elements would imply additional processes which would enrich the top soil layer that supplies the river particulate load through mechanical erosion, leaving the remaining soil profile depleted in these elements with respect to Al.

Several kinds of fractionation processes are likely to occur simultaneously: chelation by organic particles, adsorption and coating of elements on fine particles, biological accumulation in organic particles, and mechanical fractionation. Evidence of this latter process has been already found (Martin et al., 1973; Förstner, 1977; Gibbs, 1977). As the fine material, in which trace metals are highly concentrated, is washed away during the erosion process and carried by rivers, a resulting depletion may occur in the remaining material.

Steady-state system and additional sources. A steady-state system implies that natural sources other than continental erosion contribute to the material carried by rivers. These sources can be volcanic dust and sea-salt particles produced by bubbles bursting at the air-sea interface which reach the continent surface through atmospheric fallout. Studies of the composition of atmospheric particulate matter in remote areas such as the North Atlantic Ocean and the South Pole, indicate that aerosols are obviously enriched in certain elements. Cu, Sb, Pb, Br, Cd, Zn, As, Ag, Se, Hg are highly enriched in the marine atmosphere, relative either to bulk seawater or to average crustal material (Duce et al., 1975, 1976; Buat-Menard and Chesselet, 1978).

As previously mentioned, volcanoes could be a possible source of enriched elements. Mroz and Zoller (1975) found that the Heimaey eruption in Iceland has produced a significant amount of aerosols highly enriched in Zn, Sb, Br with respect to the earth's crust. Similar enrichment has been found in the Kilauea fume in Hawaii (Duce et al., 1976). However the global input of this source is very difficult to compute. According to Mroz and Zoller (1975), the total mass of aerosols from volcanic origin would be between 1 and 20% of the global aerosols production.

The major origin of atmospheric particles is the production of aerosols at the air/sea interface. The global flux of such particles, with radii less than $20\ \mu$, is estimated to be $10^{15}\ \text{g year}^{-1}$ (Erikson, 1959), of which 10 to 30% finally reach the continents. If such an input is considered to balance actual river excess of elements such as Cu or Zn, it is necessary to attribute to these particles of oceanic origin very high elemental contents, some percents, which would correspond to enrichment factors relative to bulk seawater of more than 10^4 . Although not impossible, it must be noted that such enrichment factors are two orders of magnitude higher than those measured with the Bubble Interface Microlayer Sampler (BIMS) by Duce et al. (1976) which can

be considered as representative for the marine part of atmospheric particle flux notwithstanding the anthropogenic and crustal weathering components.

Comparison of river suspended matter with oceanic sediments

In order to gain insight into marine sedimentation processes, it is worthwhile to compare the chemical composition of river suspended sediment with that of deep-sea clays and oceanic suspended matter. However, this comparison can be biased by several factors:

(1) River-borne material has a wide range of particle size which can be modified through deposition in estuaries and nearshore areas. For instance a recent study of the Mississippi delta (Trefry and Presley, 1976) has shown that more than 90% of the river-borne sediment is deposited in an area around the delta that is less than 1% of the area of the Gulf of Mexico.

This process can enhance the proportion of the smaller grain-sized fraction of the actual river sediment input to the open ocean (Postma, 1967); as shown previously this fraction will exhibit higher trace-element concentrations due to a larger specific surface area (Martin et al., 1973).

(2) The overall effect of adsorption-desorption processes occurring in estuaries is poorly known. However, many elements are conservative during estuarine mixing (e.g., U, B, . . .) (Martin and Meybeck, 1978; Fanning and Maynard, 1978), while little field evidence for desorption has been given except for Ba (Edmond, 1978) and some radioactive elements (Evans and Cutshall, 1973). Finally, whenever precipitation onto particulates occurs, it usually affects chemical elements which have a low DTI value, such as Fe and lanthanides, so that the concentration of river particulates is not greatly altered (Martin et al., 1976; Figueres et al., 1978).

(3) Finally, further oceanic processes such as dissolution during settling, diffusion and biological recycling at the sediment-water interface may change the original elemental concentration of river-borne particulates.

Despite these difficulties, an attempt to compare the average concentrations in river particulate and oceanic sediments is made in Table III. The reference data used for deep-sea clay are those compiled or computed by the following authors: Wedepohl (1960), Horn and Adams (1966), Hogdahl (1970), Fairbridge (1972), Piper (1974), Chester and Aston (1976). For oceanic suspended matter we used the data of Darcourt-Rieg (1973), Chester and Stoner (1975), and Buat-Menard and Chesselet (1978, 1979).

Comparison between river particulate matter and deep-sea clays

Various categories of elements have been differentiated:

(1) Elements which have similar concentrations in river suspended matter and in deep-sea clays.

These elements are the following: lanthanides, Sc, V, Ta, Rb, P, Co, Fe, Ga, Ti, Si, Al. One must point out the striking similarity of Si-Al concentrations which allows a meaningful comparison of the two types of materials,

excluding any matrix effect. The oceanic distribution of these various elements is obviously controlled by river input. All of them are likely to be "lattice-held" (Chester and Aston, 1976).

(2) Elements in "excess" in river suspended sediment

Within this category one finds Ca, Sb and Zn. Calcium is partly carried to the ocean as CaCO_3 particles which can eventually be dissolved below the carbonate compensation layer. For Sb and Zn two hypotheses may be considered. A present-day, non-steady-state sedimentation model implies that the input in river suspended matter exceeds the output in deep-sea clays. This again raises the problem of the anthropogenic origin of these elements in river suspended sediment. However it is important to note that neither Pb nor V, which are typically representative of an anthropogenic origin, are higher in river suspended sediment than in deep sea clays.

A steady-state sedimentation system can also be considered. There is now evidence that zinc may have a nutrient-like behaviour and is mobilized out of the bottom sediment, most likely through biological processes, to the water column (Bruland et al., 1978).

(3) Elements in "excess" in deep-sea clays

Within this category one must consider first those elements which are depleted in river suspended sediment with regard to the surficial rocks (Br, Mo, B, Na, As, Ba, etc.). They correspond to the elements which have a high DTI in rivers. Their concentration in the deep-sea clay would be enhanced through abiological (e.g., B) or biological processes (e.g., Br) so as to balance the total river input (i.e., dissolved + particulate). In order to determine whether they are actually in excess or not, it would be necessary to consider their removal from the solution as well as the deep-sea-clay sedimentation rate and diffusive processes at the benthic boundary layer. The data needed are too scanty and/or approximate to allow such a model to be meaningful.

The second category concerns the elements which have a low DTI in rivers. In that case they can be directly compared to deep-sea clays. Any excess can then be ascribed to an enrichment which occurred at some time in their history. Those elements are essentially Mn, Co, Ni and Cu, and they would be essentially in a "non lattice-held" position (Chester and Messiha-Hanna, 1970).

With regard to manganese, under anaerobic conditions occurring in estuarine and nearshore bottom sediments, fairly soluble sulfide compounds are formed and are subject to release (Evans et al., 1977; Sundby, 1977). Once they reach the aerated water column, they form highly insoluble oxides which might be supplied to the deep-sea sediments (K. K. Turekian, pers. comm., 1974). These manganese oxides may be subsequently enriched in various trace metals for which they behave as efficient scavengers.

The elements in excess in deep-sea clays also correspond to those found in excess in mid-oceanic deep sediment by Chester and Messiha-Hanna (1970). Another possible origin for this excess in deep-sea clays could be in volcanic emanations which were considered as early as 1960 by Wedepohl. Further

evidence of volcanic origin has been given for various elements such as U, Fe, V (Boström and Fisher, 1971), but as mentioned above, these latter elements can also be of terrigenous origin. In their review paper, Chester and Aston (1976) concluded on "the rather insignificant role played by volcanic sources in the budget of solid brought to the world ocean in general", while in some "regions (e.g., those adjacent to volcanic regions or areas of active sea-floor spreading) volcanic and hydrothermal sources are extremely important for the provision of sedimentary material."

Turekian (1965, 1967) stated that the excess of trace elements results to a large extent from a differential transport of pelagic and non-pelagic particulates to and within the ocean. Such a statement supposes that a large proportion of the excess of Cu, Ni, Co and Mn is acquired in the river environment. The concentrations of these elements found in river suspended matter are too low to support this assumption.

Comparison of river particulate material with oceanic suspended matter

At this stage it is worthwhile comparing the river suspended sediment with the oceanic one. Comparison with the elemental concentrations in the suspended matter from the euphotic zone (Chester and Stoner, 1975) is difficult since the Al content of these particles unfortunately is unknown. However, the elemental concentrations appear to be of the same order of magnitude for all the measured elements, including those in excess in deep-sea clays.

Finally, a comparison of our data with deep-oceanic suspended-matter concentrations measured by Buat-Menard and Chesselet (1978, 1979) (Table III) shows very much higher elemental contents in this material, especially if these data are normalized to Al. The striking analogy of the enrichment factors they have determined with those found in marine aerosols raises the question of an atmospheric control of deep-ocean suspended-matter composition.

In an attempt to solve this important problem, Buat-Menard and Chesselet show that, except possibly for lead, concentrations of heavy metals in excess in the North Atlantic particulate matter cannot be of anthropogenic origin. They consider that natural processes taking place in the ocean itself are necessary to explain the observed enrichments of Cr, Cu, Zn, Se, Sb, Au, As and Hg. Cobalt, which follows the Al-Sc-Fe group, would have a predominantly atmospheric origin.

A subsidiary conclusion of their paper is that the vertical flux of oceanic particulate matter cannot explain more than 10% of the Al deposited in deep-sea clays, requiring another source of sediment such as bottom transport of shelf material. This conclusion is in very good agreement with our own data. The elemental contents found in deep-sea clays can be interpreted as resulting from a mixing of very rich open-ocean suspended material with less-enriched terrigenous material. However, for those elements which are drastically enriched in oceanic suspended matter, particularly those which also have a higher concentration in river particulates (e.g., Sb, Zn) than in deep sea

clays, this dilution effect cannot explain the lower concentrations found in deep-sea clays. As mentioned previously, it is necessary that significant remobilization processes take place at the benthic boundary layer in order to balance the input of excess elements to the deep-sea clays.

CONCLUSIONS

Although the 20 major rivers used in the estimate of the river particulate matter represent only 15% of the world rivers' solid load and despite the variability of certain elements and the scarcity of data for certain others, the following conclusions can be made.

(1) Major element variations in river particulate matter can be fully explained by weathering types and the balance between weathering rate and river transport.

(2) As a result of chemical erosion, which globally represents 25% of the total river load, Al, Fe and Ti are enriched in river suspended matter relative to the average parent rock, while Na, Ca, Mg, Sr are strongly depleted. These changes in river particulates are directly related to the relative importance of dissolved and particulate transports in rivers. These ratios have been computed for all elements on the basis of literature data for the average dissolved contents.

(3) Dissolved transport is a major process for Br, I, S, Cl, Ca, Na, Sr and is still important for Li, N, Sb, As, Mg, B, Mo, F, Cu, Zn, Ba and K. For P, Ni, Si, Rb, U, Co, Mn, Cr, Th, Pb, V and Cs, more than 90% of the total load is carried by river particulates, while Fe, Al, and the rare earths are almost exclusively carried as particulates.

(4) Relationships between weathering and river transport are usually studied by comparison between river particulates and the surficial rock exposed to erosion. A fractionation factor is defined with regard to a conservative element, usually Al. However this approach is only justified for the elements for which river dissolved transport is negligible, say less than 10%. For all other elements this comparison must be made on total fluxes (dissolved + particulate).

(5) If it is assumed that weathering has reached a steady state at the earth's surface, i.e., river material corresponds to present weathering conditions and is not partially derived from past climatic conditions, then the theoretical quantity of weathered material can be estimated on the basis of the elemental ratio in average suspended matter and in average surficial rock, provided that the chosen element is conservative and poorly soluble. Al has been used for that purpose, the ratio is equal to 1.36. The present river load of solids to the ocean is around $15.5 \cdot 10^{15} \text{ g year}^{-1}$ which should then correspond to the weathering of $21.1 \cdot 10^{15} \text{ g year}^{-1}$ of fresh rock and to a river transport of $5.6 \cdot 10^{15} \text{ g year}^{-1}$ of dissolved substances derived from weathering. This is, however, higher than present estimates.

(6) Observed and theoretical river fluxes have been computed for 40 elements. Dissolved fluxes are derived from a literature review. For most elements, either easily or poorly mobilized (B, Ba, Ca, Ce, Co, Cr, Cs, Eu, Fe, Ga, K, La, Mg, Mn, Na, Nd, Rb, Sc, Si, Sm, Sr, Tb, Ti, Th, U, V, and Yb) the total amount of material carried by rivers is equivalent to the theoretical value.

(7) Additional fluxes have been observed for some elements, either easily mobilized (Br, Cu, Mo, Sb, Zn) or poorly mobilized such as Pb. An excess is also possible for Ni and P although this is uncertain due to a lack of sufficient data. It is striking to note that many of these elements are also highly enriched in the atmospheric aerosols, of marine origin and of volcanic origin, or of anthropogenic origin (Mroz and Zoller, 1975; Duce et al., 1975, 1976; Buat-Menard and Chesselet, 1978; Lantzy and Mackenzie, 1978). These additional fluxes can be explained by a geochemical fractionation in the soil profile, which corresponds to non-steady-state weathering. In the case of a steady state between weathering and river transport, additional natural sources (volcanic dust and marine aerosols) must be looked for. Worldwide pollution can also partially explain these fluxes. However, none of these processes can fully account for the observed excess transport and most probably various single or multiple causes must be considered for each given element.

(8) A comparison of the chemical compositions of river suspended sediments with those of deep-sea clays shows, on the whole, fairly good agreement, which stresses the major influence of river input on deep-sea clay composition.

(9) Some elements such as Zn have been observed in "excess" in river suspended sediment or compared to deep-sea clays. If one assumes a natural origin to account for this excess, a remobilization of these elements from the bottom sediment to the water column is required to balance the terrigenous input.

(10) Deep sea-clays are "enriched" in Br, Mo, B, Na, As and Ba relative to river particulate matter. For these elements which are mainly carried by rivers in a dissolved form, it is likely that elemental contents in deep ocean sediments are enhanced by various processes transferring the input dissolved material to the bottom deposit.

(11) Other elements transported less in the dissolved form: Co, Cu, Mn, and Ni are actually enriched in deep-sea clays. It is likely that they represent an admixture in various proportions of river-borne eroded material and marine biomass, with an additional supply of volcanogenic and atmospheric material.

ACKNOWLEDGEMENTS

We would like to express our appreciation to R. Chesselet and K. K. Turekian for their helpful criticism of the first draft of this paper. We thank

J. P. Carbonnel, S. Krishnaswamy, H. Sioli and P. J. De Petris, for providing us with some precious samples and J. C. Phillipot, C. Kulbicki and P. Blanc for their analytical assistance.

Financial support for this study has been provided by the Centre National de la Recherche Scientifique.

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